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## (54) LITHIUM PRIMARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium primary cell which has a high output, a long life and a high safety because this has a high discharge capacity and a high energy density.

SOLUTION: This is the lithium primary cell provided with a positive electrode characterized that at least one kind of metal oxide selected from a group consisting of titania, alumina, zinc oxide, chromium oxide, lithium oxide, nickel oxide, copper oxide and iron oxide is dispersed among particles of manganese

dioxide, a negative electrode, and an electrolytic solution

composed of an aprotic organic solvent and a supporting

electrolyte wherein a phosphazene derivative expressed by

formula (1) and/or an isomer of the phosphazene derivative is

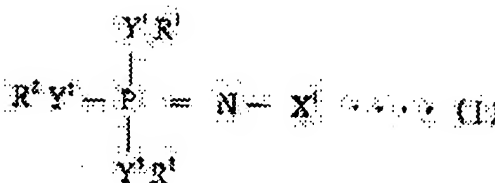
added. In the formula, R1, R2 and R3 express a monovalent

substituent or halogen element. X1 expresses a substituent

including at least one kind of element selected from a group consisting of carbon, silicon,

germanium, tin, nitrogen phosphorus, arsenic, antimony, bismuth, oxygen, sulfur, selenium, tellurium

and polonium. Y1, Y2 and Y3 express a divalent coupling group, a divalent element or a single bond.



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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** Especially this invention relates to the lithium primary cell which is excellent in discharge capacity and an energy density about a lithium primary cell.

**[0002]**

**[Description of the Prior Art]** In recent years, with the rapid advance of electronics, especially, as a power source of small electronic equipment, it is small and lightweight and the cell of long lasting and a high energy consistency is called for. On the other hand, the lithium primary cell which uses a manganese dioxide as a positive electrode and uses a lithium as a negative electrode has the lowest electrode potential of a lithium in a metal, since the electric capacity per unit volume is large, it is known as one of the cells which has a high energy consistency, and many kinds of things are studied actively.

**[0003]** On the other hand, even if a blowout etc. arises in a pneumatic tire, the run flat tire which can carry out continuation transit of the considerable distance to the location which can perform repair and repair is developed. When the internal pressure of a tire is measured and it becomes the internal pressure below fixed in connection with this, forming the internal pressure alarm which transmits the signal which tells abnormalities in said run flat tire is proposed.

**[0004]** Here, as a power source of an internal pressure alarm, small [ above-mentioned ] and the lithium primary cell which is lightweight, and uses the manganese dioxide of long lasting and a high energy consistency as a positive electrode, and uses a lithium as a negative electrode are used.

**[0005]** Moreover, in a lithium primary cell, although the lithium is used abundantly, in order that this lithium may react violently with the compound which has activity protons, such as water or alcohol, as an ingredient which forms a negative electrode, the electrolyte used is restricted to a nonaqueous solution or a solid electrolyte. Since ion conductivity of a solid electrolyte is low, it is restricted only to the use in the low discharge current. Therefore, current and the electrolytic solutions generally used are aprotic organic solvents, such as an ester system organic solvent.

**[0006]**

**[Problem(s) to be Solved by the Invention]** However, since advanced features of an internal pressure alarm are requested as transmitting many information on a tire other than tire internal pressure and power consumption increases in connection with it, in having used the existing lithium primary cell for the power source of an internal pressure alarm, the problem that a life is short and exchange is needed for a short period of time arises.

**[0007]** Moreover, negative-electrode ingredients were a lithium metal and a lithium alloy, when obturation of a cell was imperfect since it is very high activity, and moisture invaded to moisture, a negative-electrode ingredient and water reacted, it carried out generating hydrogen or igniting etc., and there was a problem that danger was high. Furthermore, since a lithium metal was a low-melt point point (about 170 degrees C), when the high current flowed rapidly at the time of a short circuit etc., the cell generated heat unusually and it also had the problem of causing the very dangerous situation of a cell fusing. Furthermore, the electrolytic solution which uses an organic solvent as the base with generation of heat of the cell mentioned above evaporated and decomposed, and the problem that generated gas or a burst and ignition of a cell took place by the gas which occurred etc. also had it. Furthermore, also in the lithium primary cell which originally does not assume charge, there might be charge by the operation mistake and there was also a problem of causing ignition in such a case.

**[0008]** Then, since discharge capacity and the energy density of this invention are high, it aims long lasting at

offering a lithium primary cell with high safety by high power.

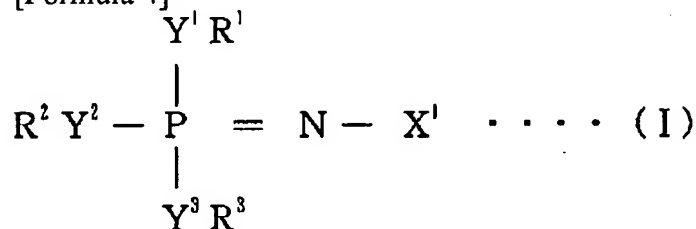
[0009]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for a lithium primary cell long lasting at high power with high discharge capacity and energy density being obtained by adding the isomer of a phosphazene derivative and/or a phosphazene derivative to the electrolytic solution while improving the manganese dioxide of a positive electrode in the lithium primary cell which uses a manganese dioxide as a positive electrode, as a result of inquiring wholeheartedly, in order to solve said technical problem.

[0010] Namely, this invention <1> It is the lithium primary cell characterized by having the electrolytic solution which consists of the positive electrode with which it comes to distribute at least one sort of metallic oxides chosen from the group which consists of titanium oxide, an alumina, a zinc oxide, chromic oxide, lithium oxide, nickel oxide, copper oxide, and an iron oxide between the particles of a manganese dioxide, a negative electrode, an aprotic organic solvent with which the isomer of a phosphazene derivative and/or a phosphazene derivative was added, and a supporting electrolyte.

[0011] <2> Said phosphazene derivative is a lithium primary cell given in the above <1> characterized by what it has the viscosity below 100 mPa-s (100cP) in 25 degrees C, and is expressed with the following type (I) or the following formula (II).

[Formula 4]



(R1, R2, and R3 express the substituent or halogen of monovalence among a formula.) X1 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, an arsenic, antimony, a bismuth, oxygen, sulfur, a selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists of a polonium. Y1, Y2, and Y3 express a divalent connection radical, a divalent element, or single bond. (NPR42) n ... (II) (R4 expresses the substituent or halogen of monovalence among a formula.) n expresses 3-15.

[0012] <3> The phosphazene derivative expressed with the above-mentioned formula (II) is a lithium primary cell given in the above <2> characterized by what is expressed with the following type (III).

(NPF2) n ... (III) (n expresses 3-13 among a formula.)

[0013] <4> The phosphazene derivative expressed with the above-mentioned formula (II) is a lithium primary cell given in the above <2> characterized by what is expressed with the following type (IV).

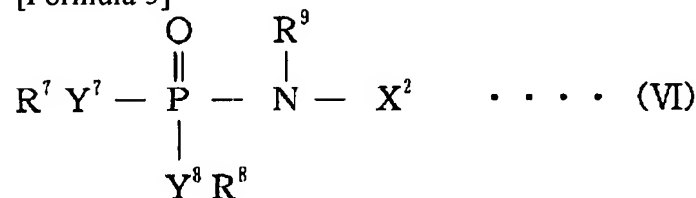
(NPR52) n ... (IV) (the inside of a formula, and R5 -- the substituent or fluorine of monovalence -- expressing -- all -- at least one of R5 is the substituent or fluorine containing a fluorine of monovalence, and n expresses 3-8.) However, no R5 is a fluorine.

[0014] <5> Said phosphazene derivative is a solid-state in 25 degrees C, and is a lithium primary cell given in the above <1> characterized by what is expressed with the following type (V).

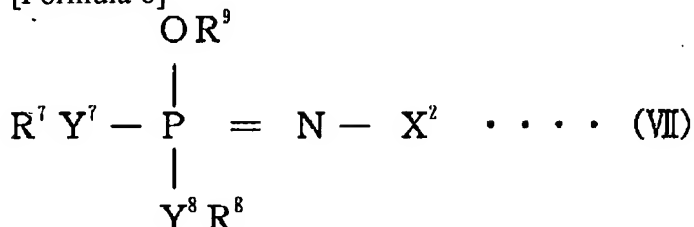
(NPR62) n ... (V) (R6 expresses the substituent or halogen of monovalence among a formula.) n expresses 3-6.

[0015] <6> Said isomer is a lithium primary cell given in the above <1> characterized by being the isomer of the phosphazene derivative which is expressed with the following type (VI) and is expressed with the following type (VII).

[Formula 5]



[Formula 6]



(Formula (VI) And (VII) it sets and R7, R8, and R9 express the substituent or halogen of monovalence.) X2 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, an arsenic, antimony, a bismuth, oxygen, sulfur, a selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists of a polonium. Y7 and Y8 express a divalent connection radical, a divalent element, or single bond.

[0016] <7> Said metallic oxide is a lithium primary cell given in any of <6> they are from the above <1> characterized by being a titanium dioxide.

<8> The mass of said metallic oxide is a lithium primary cell given in any of <7> they are from the above <1> characterized by being 0.5% to 4% to the mass of said manganese dioxide.

[0017]

[Embodiment of the Invention] Below, this invention is explained at a detail. The lithium primary cell of this invention is equipped with a positive electrode, a negative electrode, and the electrolytic solution, and is equipped with the member usually used by the technical field of lithium primary cells, such as a separator, if needed.

[0018] The positive electrode which constitutes the lithium primary cell of this invention consists of a manganese dioxide and a metallic oxide distributed between the particles of this manganese dioxide, and contains the additive usually used by the technical field of lithium primary cells, such as electric conduction material and a binder, if needed.

[0019] The manganese dioxide used by this invention may be electrochemistry composition, or may be chemosynthesis. Also in the ingredient usually used as a positive electrode of a lithium primary cell, discharge potential is high capacity highly, and this manganese dioxide is excellent in safety and the wettability of the electrolytic solution, and further excellent also in respect of cost. The particle size of this manganese dioxide is 1-60 micrometers, and is 20-40 micrometers preferably. Since the amount of positive active material which packing worsens at the time of positive-electrode plied timber (it consists of manganese-dioxide, electric conduction material, and binder) shaping, or is contained in unit volume will decrease, and discharge capacity may decrease, it is not [ be / it / if / particle size exceeds less than 1 micrometer or 60 micrometers, ] desirable.

[0020] As a metallic oxide used for this invention, titanium oxide, an alumina, a zinc oxide, chromic oxide, lithium oxide, nickel oxide, copper oxide, and an iron oxide may be mentioned, and these may be independent one sort or may be two or more sorts of concomitant use.

[0021] As for this metallic oxide, it is desirable that it is a very detailed particle, and the particle size is 10nm - 1 micrometer, and is 20nm - 60nm preferably. A less than 10nm particle is not desirable, in order that the amount of the manganese dioxide as positive active material with which particle size is contained in per unit volume when composition is difficult and exceeds 1 micrometer industrially may decrease and the amount of energy per unit volume may decrease.

[0022] In this invention, since the metallic oxide is distributed between the particles of a manganese dioxide, a clearance is generated between manganese-dioxide particles. Since the electrolytic solution can infiltrate into this clearance efficiently, the touch area of the electrolytic solution and a manganese dioxide increases, the utilization factor of a manganese dioxide increases as the result, and discharge capacity and energy density improve. Especially titanium oxide is desirable also in the metallic oxide which forms a clearance between manganese-dioxide particles, and what titanium oxide does not have it not only contributing to the stability of a cell, but not checking cell electrode reaction of a lithium primary cell and absorbing moisture effectively and reducing conductivity remarkably by addition for (internal resistance does not rise) is mentioned as the reason.

[0023] 0.5 to 4% of the mass of the metallic oxide in said positive electrode is desirable to the mass of a manganese dioxide. In order that the particle front face of a manganese dioxide may be covered with a metallic

oxide and the touch area of the electrolytic solution and a manganese dioxide may decrease, it is not desirable at the same time the amount of manganese dioxides per unit volume will decrease, if the effectiveness that the mass of a metallic oxide distributes a metallic oxide between the particles of a manganese dioxide as it is less than 0.5%, and it forms a clearance to the mass of a manganese dioxide is not enough and exceeds 4%.

[0024] As electric conduction material, acetylene black etc. is mentioned to the positive electrode which constitutes the lithium primary cell of this invention among the additives added if needed, and polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), etc. are mentioned to it as a binder. the blending ratio of coal same when using these additives as usual, for example, the powder:electric conduction material for positive electrodes, -- it can blend by :binder =8:1:1-8:1:0.2 (mass ratio).

[0025] As a configuration of a positive electrode, there is especially no limit and it can be suitably chosen from configurations well-known as an electrode. For example, the shape of the shape of a sheet and a cylindrical shape, a tabular configuration, a spiral configuration, etc. are mentioned.

[0026] As an ingredient of the negative electrode which constitutes the lithium primary cell of this invention, a lithium alloy besides the lithium metal itself etc. is mentioned. As a metal which builds a lithium and an alloy, Sn, Pb, aluminum, Au, Pt, In, Zn, Cd, Ag, Mg, etc. are mentioned. Also in these, the numerousness of reserves and a toxic viewpoint to aluminum, Zn, and Mg are desirable. These ingredients may be used by the one-sort independent, and may use two or more sorts together. As a configuration of a negative electrode, there is especially no limit and it can be suitably chosen from the configuration of the positive electrode mentioned above, and the same well-known configuration.

[0027] The electrolytic solution of the lithium primary cell of this invention consists of an aprotic organic solvent with which the isomer of a phosphazene derivative and/or a phosphazene derivative was added, and a supporting electrolyte. Since the negative electrode of a lithium primary cell consists of a lithium or a lithium alloy as mentioned above, reactivity with water is very high, therefore water and the aprotic organic solvent which does not react are used for a solvent.

[0028] As an aprotic organic solvent, although there is especially no limit, an ether compound, an ester compound, etc. are mentioned from a viewpoint which stops the viscosity of the electrolytic solution low. Specifically, 1, 2-dimethoxyethane (DME), a tetrahydrofuran, dimethyl carbonate, diethyl carbonate, diphenyl carbonate, ethylene carbonate, propylene carbonate (PC), gamma-butyrolactone (GBL), gamma-valerolactone, methylethyl carbonate, ethyl methyl carbonate, etc. are mentioned suitably. Chain-like ether compounds, such as chain-like ester compound [ , such as cyclic-ester compounds, such as propylene carbonate and gamma-butyrolactone, dimethyl carbonate, and methylethyl carbonate, ], 1, and 2-dimethoxyethane, etc. are suitable also in these. Specific inductive capacity is suitable for especially an annular ester compound at the point of excelling in the solubility of a supporting electrolyte (lithium salt) mentioned later highly, and on the other hand, since chain-like an ester compound and an ether compound are hypoviscosity, they are suitable in respect of hypoviscosity-izing of the electrolytic solution. These may be used by the one-sort independent and may use two or more sorts together.

[0029] That what is necessary is just what is usually used as the ion source of a lithium ion as a supporting electrolyte, as the ion source of this lithium ion, although there is especially no limit, lithium salt, such as  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiAsF}_6$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ , and  $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$ , is mentioned suitably, for example. These may be used by the one-sort independent and may use two or more sorts together.

[0030] As a content of the supporting electrolyte in the electrolytic solution, 0.2-1 mol is desirable to solvent component 1L of the electrolytic solution, and 0.5-1 mol is more desirable. While a content cannot secure conductivity with the electrolytic solution sufficient in the case of less than 0.2 mols but may cause trouble to the discharge property of a cell, when it exceeds one mol Since sufficient conductivity of the electrolytic solution cannot be secured like the above-mentioned since the viscosity of the electrolytic solution rises and sufficient mobility of a lithium ion cannot be secured, but solution resistance goes up as a result, trouble may be caused to a pulse discharge and a low-temperature property.

[0031] In this invention, it is as follows as a reason for adding a phosphazene derivative to the electrolytic solution. That is, as mentioned above, between the particles of a manganese dioxide, while distributing a specific metallic oxide, by adding the isomer of a phosphazene derivative and/or a phosphazene derivative to an aprotic organic solvent, the discharge capacity and the energy density of a lithium primary cell can be raised,

and a long lasting lithium primary cell is obtained by high power.

[0032] Moreover, the aprotic organic solvent in a lithium primary cell is conventionally set to the electrolytic solution used as the base. When a high current flows rapidly at the time of a short circuit etc. and a cell generates heat unusually, it evaporates and decomposes. Gas occurs or Since a burst and ignition of a cell take place with the gas and the heat which were generated, danger is high. Although the danger that the spark produced at the time of a short circuit will ignite to the electrolytic solution, and will cause ignition and a burst is also high, if the phosphazene derivative contains in the electrolytic solution of these former Even if evaporation, disassembly, etc. of the electrolytic solution [ in / comparatively / low temperature ] of 200-degree-C or less extent are controlled, the danger of ignition and ignition is reduced and there is ignition inside a cell by melting of a negative-electrode ingredient etc., the danger of a spreading fire will be low. Furthermore, since Lynn has the operation which controls chain decomposition of the polymeric materials which constitute a cell, the danger of said ignition and ignition is reduced effectively. Furthermore, if the phosphazene derivative contains in the conventional electrolytic solution, it will become possible to offer the lithium primary cell excellent also in low temperature and an elevated-temperature property.

[0033] Furthermore, phosphazene has only the potential window which fully functions as a primary cell, and does not decompose it by discharge. Moreover, the phosphazene which the phosphazene containing a halogen (for example, fluorine) functions as a scavenger of an activity radical at the time of emergency combustion, and has an organic substituent also has the screening effect of oxygen in order to generate carbide (char) on pole material and a separator at the time of combustion. In addition, also when a user charges accidentally, since phosphazene has the depressor effect of dendrite generation, as compared with an additive-free system, safety becomes high more.

[0034] In addition, in this invention, the oxygen-index measurement according to JIS K 7201 estimated the danger of ignition and ignition. In addition, the value of the minimum oxygen density expressed with the percent by volume which needs an oxygen index for an ingredient to maintain combustion under the predetermined test condition of the convention to JIS K 7201 is said, that an oxygen index is low means that the danger of ignition and ignition is high, and that an oxygen index is high on the contrary means that the danger of ignition and ignition is low. This application estimated the danger of ignition and ignition with the limiting oxygen index according to the above-mentioned oxygen index.

[0035] As for the electrolytic solution with which the isomer of a phosphazene derivative and/or a phosphazene derivative was added, it is desirable that a limiting oxygen index is more than 21 volume %. When a limiting oxygen index is under 21 volume %, the depressor effect of ignition and ignition is not sometimes enough. Under an ambient condition, since an oxygen index is equivalent to 20.2 volume %, limiting-oxygen-index 20.2 volume % means burning in atmospheric air. Wholeheartedly, by examination, when it was more than limiting-oxygen-index 21 volume %, it was more than 23 volume % about self-extinguishing and it was more than 25 volume % about fire retardancy, artificers' thing for which it has incombustibility was found out.

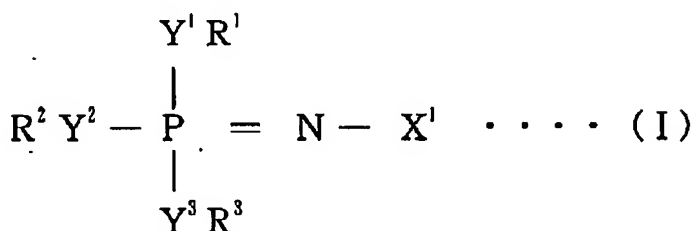
[0036] In addition, the self-extinguishing, fire retardancy, and incombustibility written here Define as the approach based on UL94 HB method, infiltrate the electrolytic solution of 1.0 ml into a noncombustible quartz fiber, and a 127mmx12.7mm test piece is produced. It digests, while the flame which lit is 25-100mm Rhine, when this test piece is lit under atmospheric environment. And the case where ignition is not accepted in a falling object from a network, either is made into those with self-extinguishing. Make the case where the flame which lit did not reach to 25mm Rhine of equipment, and ignition is not accepted in a falling object from a network, either into a fire-resistant \*\*\*\*, and let the case (0mm of combustion length) where ignition is not accepted be those with noncombustible.

[0037] As a phosphazene derivative added to an aprotic organic solvent, although there is especially no limit, viscosity is comparatively low and the phosphazene derivative which the viscosity in 25 degrees C is below 100 mPa-s (100cP), and is expressed with a degree type (I) or a degree type (II) from a viewpoint which dissolves a supporting electrolyte good is desirable.

[0038]

[Formula 7]





(R1, R2, and R3 express the substituent or halogen of monovalence among a formula.) X1 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, an arsenic, antimony, a bismuth, oxygen, sulfur, a selenium, a tellurium, and the organic radical containing at least one sort of the element chosen from the group which consists of a polonium. Y1, Y2, and Y3 express a divalent connection radical, a divalent element, or single bond.

(NPR42) n ... (II) (R4 expresses the substituent or halogen of monovalence among a formula.) n expresses 3-15.

[0039] It is required to be below 100 mPa-s (100cP) as viscosity in 25 degrees C of the phosphazene derivative expressed with a formula (I) or a formula (II), and below 20 mPa-s (20cP) is desirable. If viscosity exceeds 100 mPa-s (100cP), it will be hard coming to dissolve a supporting electrolyte, the wettability to a positive-electrode ingredient, a separator, etc. will fall, ion conductivity will fall remarkably according to increase of the viscous drag of the electrolytic solution, and it will become deficient in performance in the use under low temperature services, such as below the freezing point, especially.

[0040] In a formula (I), as R1, R2, and R3, if it is the substituent or halogen of monovalence, there will be especially no limit. It is the point which an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. are mentioned, and can hypoviscosity-ize the electrolytic solution also in these as a substituent of monovalence, and an alkoxy group is desirable. On the other hand, as a halogen, a fluorine, chlorine, a bromine, etc. are mentioned suitably. The substituent of the same class is sufficient as all of R1-R3, and the substituent of the class from which some of them differ is sufficient as them.

[0041] As said alkoxy group, alkoxy permutation alkoxy groups, such as a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. and a methoxyethoxy radical, a methoxyethoxy ethoxy radical, etc. are mentioned, for example. Also in these, all are suitable for a methoxy group, an ethoxy radical, a methoxyethoxy radical, or a methoxyethoxy ethoxy radical as R1-R3, and it is suitable that the viewpoint of hypoviscosity and a quantity dielectric constant to all are especially a methoxy group or an ethoxy radical.

[0042] As said alkyl group, a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, etc. are mentioned. As said acyl group, a formyl group, an acetyl group, a propionyl radical, a butyryl radical, an isobutyryl radical, a valeryl radical, etc. are mentioned. As said aryl group, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As for the hydrogen element in the substituent of such monovalence, permuting by the halogen is desirable, and a fluorine, chlorine, a bromine, etc. are suitably mentioned as a halogen.

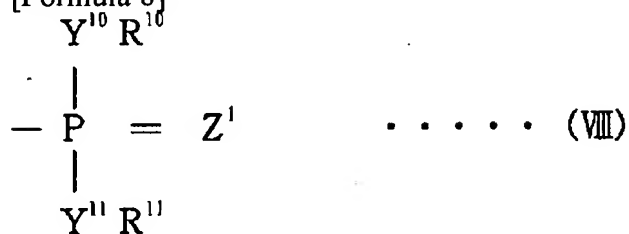
[0043] In a formula (I), as a divalent connection radical expressed with Y1, Y2, and Y3 For example, oxygen besides two CH(s), sulfur, a selenium, nitrogen, boron, aluminum, A scandium, a gallium, an yttrium, an indium, a lanthanum, a thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Lynn, Vanadium, an arsenic, niobium, antimony, a tantalum, a bismuth, chromium, The divalent connection radical containing at least one sort of the element chosen from the group which consists of molybdenum, a tellurium, a polonium, a tungsten, iron, cobalt, and nickel is mentioned. The divalent connection radical containing at least one sort of the element chosen from the group which consists of two CH(s) and oxygen, sulfur, a selenium, and nitrogen also in these is desirable, and especially the divalent connection radical containing the element of sulfur and/or a selenium is desirable. Moreover, Y1, Y2, and Y3 may be divalent elements, such as oxygen, sulfur, and a selenium, or single bond. The same class is sufficient as all of Y1-Y3, and the class from which some differ mutually is sufficient as them.

[0044] In a formula (I), the organic radical which contains at least one sort of carbon, silicon, nitrogen, Lynn, oxygen, and the element chosen from the group which consists of sulfur from a viewpoint of consideration of harmful nature, an environment, etc. as X1 is desirable. The organic radical which has the structure expressed with a degree type (VIII), (IX), or (X) among these organic radicals is more desirable.

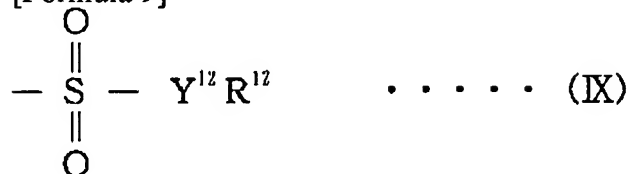


[0045]

[Formula 8]



[Formula 9]



[Formula 10]



However, in a formula (VIII), (IX), and (X), R10-R14 express the substituent or halogen of monovalence. Y10-Y14 express a divalent connection radical, a divalent element, or single bond, and Z1 expresses a divalent radical or a divalent element.

[0046] In a formula (VIII), (IX), and (X), each the substituent or halogen of the same monovalence is mentioned suitably as R1-R3 in a formula (I) described as R10-R14. Moreover, the class from which the respectively same class is sufficient and some differ mutually in the same organic radical is sufficient as these. It may join together mutually and R10 and R11 of a formula (VIII), and R13 and R14 of a formula (X) may form the ring.

[0047] In a formula (VIII), (IX), and (X), the same divalent connection radical or same divalent element etc. is mentioned, and similarly, when it is a radical containing the element of sulfur and/or a selenium, especially in order that the danger of ignition and ignition of the electrolytic solution may decrease, it is as desirable as Y1-Y3 in a formula (I) described as a radical expressed with Y10-Y14. The class from which the respectively same class is sufficient and some differ mutually in the same organic radical is sufficient as these.

[0048] It sets at a ceremony (VIII) and they are two CH(s) and CHR (R expresses an alkyl group, an alkoxyl group, a phenyl group, etc.) as Z1, for example. the following -- the same . oxygen besides a radical and NR radical, sulfur, a selenium, boron, and aluminum -- A scandium, a gallium, an yttrium, an indium, a lanthanum, a thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Lynn, Vanadium, an arsenic, niobium, antimony, a tantalum, a bismuth, chromium, The divalent radical containing at least one sort of the element chosen from the group which consists of molybdenum, a tellurium, a polonium, a tungsten, iron, cobalt, and nickel etc. is mentioned. The divalent radical containing at least one sort of the element chosen from the group which consists of oxygen besides two CH(s), a CHR radical, and NR radical, sulfur, and a selenium also in these is desirable. In the case of the divalent radical which contains the element of sulfur and/or a selenium especially, it is desirable in order that the danger of ignition and ignition of the electrolytic solution may decrease. Moreover, Z1 may be divalent elements, such as oxygen, sulfur, and a selenium.

[0049] It is the point that the danger of ignition and ignition can be especially reduced effectively as these organic radical, and especially an organic radical including Lynn which is expressed with a formula (VIII) is desirable. Moreover, especially when an organic radical is an organic radical containing sulfur which is expressed with a formula (IX), it is desirable in respect of the formation of small interfacial resistance of the electrolytic solution.

[0050] In a formula (II), as R4, if it is the substituent or halogen of monovalence, there will be especially no

limit. It is the point which an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. are mentioned, and can hypoviscosity-ize the electrolytic solution also in these as a substituent of monovalence, and an alkoxy group is desirable. On the other hand, as a halogen, a fluorine, chlorine, a bromine, etc. are mentioned suitably, for example. As this alkoxy group, for example, a methoxy group, an ethoxy radical, a methoxyethoxy radical, a propoxy group, a phenoxy group, etc. are mentioned, and a methoxy group, an ethoxy radical, and especially n-propoxy group are desirable also in these. As for the hydrogen element in these substituents, permuting by the halogen is desirable, and a fluorine, chlorine, a bromine, etc. are suitably mentioned as a halogen.

[0051] It becomes compoundable [ the phosphazene derivative which has the solubility suitable for more suitable viscosity, and addition and mixing etc. ] by choosing suitably a formula (I), (II), R1-R4 in (VIII)- (X), R10-R14, Y1-Y3, Y10-Y14, and Z1. These phosphazene derivative may be used by the one-sort independent, and may use two or more sorts together.

[0052] It is desirable to have the substituent which contains a halogen in the molecular structure as a phosphazene derivative expressed with a formula (I) or a formula (II). If it has the substituent which contains a halogen in the molecular structure, the halogen gas guided from a phosphazene derivative will enable it more effectively to reduce the danger of ignition and ignition of the electrolytic solution also with a content smaller than the inside of numeric-value within the limits of the content of a phosphazene derivative. In addition, although generating of a halogen radical may pose a problem in the compound which contains a halogen in a substituent, such a problem is not generated in order, as for the phosphazene derivative expressed with a formula (I) or a formula (II), to form stable halogenation Lynn by the Lynn element in the molecular structure catching a halogen radical.

[0053] As a content in the phosphazene derivative of a halogen, 2 - 80 % of the weight is desirable, 2 - 60 % of the weight is more desirable, and 2 - 50 % of the weight is still more desirable. Since viscosity will become high if it exceeds 80 % of the weight while the effectiveness in which a content includes a halogen at less than 2 % of the weight may not fully show up, when it adds to the electrolytic solution, the conductivity may fall. Especially as a halogen, a fluorine, chlorine, a bromine, etc. are suitable and the viewpoint which acquires a cell property good also in this to especially a fluorine is desirable.

[0054] As a content of the phosphazene derivative expressed with the formula (I) or formula (II) to the electrolytic solution, from a viewpoint of a limiting oxygen index, more than 5 volume % is desirable, and 10 to 50 volume % is more desirable. By adjusting a content to the value of said numeric-value within the limits, the danger of ignition and ignition of the electrolytic solution is reduced effectively. In addition, although the danger of ignition is reduced effectively, the range is optimized by texture \*\*\*\*\* timely in the content which it changes with the class of supporting electrolyte to be used, or classes of electrolytic solution, and the specifically used system is most stopped by hypoviscosity, and a limiting oxygen index becomes more than 21 volume %.

[0055] Especially the phosphazene derivative expressed with a degree type (III) from a viewpoint which hypoviscosity-izes the electrolytic solution, raises the low-temperature property of a cell, and raises the degradation-proof nature and the safety of the electrolytic solution further also in the phosphazene derivative of said formula (II) is desirable.

(NPF2) n ... (III) (n expresses 3-13 among a formula.)

[0056] As a desirable reason, the phosphazene derivative expressed with the above-mentioned formula (III) is as follows. That is, in the electrolytic solution containing the supporting electrolyte used as the ester system organic solvent used for the conventional lithium primary cell, and the source of a lithium ion, when a supporting electrolyte decomposes with the passage of time and a decomposition product reacts with the water of the minute amount which exists in an organic solvent etc., the conductivity of the electrolytic solution may fall or degradation of pole material may be produced. On the other hand, if the phosphazene derivative expressed with a formula (III) by the conventional electrolytic solution is added, decomposition of a supporting electrolyte will be controlled and the stability of the electrolytic solution will improve remarkably. Generally as a supporting electrolyte, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N etc. is used, and although LiCF<sub>3</sub>SO<sub>3</sub> with low hydrolysis of the supporting electrolyte itself, Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N, and especially Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N are desirable, LiBF<sub>4</sub> and LiPF<sub>6</sub> can be suitably used according to the above-mentioned operation of phosphazene.

[0057] Moreover, the phosphazene derivative expressed with a formula (III) is a liquid of hypoviscosity in ordinary temperature (25 degrees C), and has a depression of freezing point operation. For this reason, it becomes possible to give the low-temperature property which was excellent in the electrolytic solution by adding this phosphazene derivative to the electrolytic solution, and hypoviscosity-ization of the electrolytic solution is attained and it becomes possible to offer the lithium primary cell which has low internal resistance and high conductivity. For this reason, in the low district and low stage of especially atmospheric temperature, even if it uses it under a low temperature service, it becomes possible to offer the lithium primary cell which shows the discharge property which was excellent over long duration.

[0058] In a formula (III), as n, the low-temperature property excellent in the electrolytic solution can be given, and it is the point in which hypoviscosity-izing of the electrolytic solution is possible, and 3-4 are desirable and 3 is more desirable. When the value of n is small, the boiling point can be low, and the ignition prevention property at the time of an approaching flame can be raised. On the other hand, since the boiling point becomes high as the value of n becomes large, it can be used for stability also at an elevated temperature. In order to obtain the target engine performance using the above-mentioned property, it is also possible to choose two or more phosphazene timely and to use it.

[0059] By choosing the n value in a formula (III) suitably, preparation of the electrolytic solution which has more suitable viscosity, the solubility suitable for mixing, a low-temperature property, etc. is attained. These phosphazene derivatives may be used by the one-sort independent, and may use two or more sorts together.

[0060] Although there will be especially no limit as viscosity of the phosphazene derivative expressed with a formula (III) if it is below 20 mPa-s (20 cP), from a viewpoint of conductive improvement and improvement in a low-temperature property, below 10 mPa-s (10 cP) is desirable, and below 5 mPa-s (5 cP) is more desirable. In addition, this invention -- setting -- viscosity -- a measurement-of-viscosity meter (R form viscometer Model RE500-SL --) The product made from East Machine Industry is used. 1 rpm, 2 rpm, 3 rpm, it measured every [ during 120 seconds ] with each rotational speed of 5 rpm, 7 rpm, 10 rpm, 20 rpm, and 50 rpm, rotational speed when indicated value becomes 50 - 60% was made into analysis conditions, and it asked by measuring the viscosity in that case.

[0061] Since the phosphazene derivative expressed with a formula (III) does not have the flash point, even if ignition etc. is controlled and ignition etc. produces the electrolytic solution containing this phosphazene derivative inside a cell, it will ignite and it will become possible to reduce the danger of burning and spreading on an electrolytic-solution front face.

[0062] As the total content of the phosphazene derivative expressed with the formula (III) in the electrolytic solution According to the effectiveness acquired by containing this phosphazene derivative Four kinds of contents, the 1st content which can give a "low-temperature property" suitable for the electrolytic solution, the 2nd content which can give "degradation-proof nature" suitable for the electrolytic solution, the 3rd content which can carry out "hypoviscosity-ization" of the electrolytic solution suitably, and the 4th content which can give "safety" suitably with the electrolytic solution, are mentioned.

[0063] More than 1 volume % of the 1st content of the phosphazene derivative expressed with the formula (III) in the electrolytic solution from a viewpoint of a "low-temperature property" is desirable, more than its 3 volume % is more desirable, and more than its 5 volume % is still more desirable. Unless a content fulfills 1 volume %, the congealing point of the electrolytic solution cannot be made low enough, and a low-temperature property is not enough.

[0064] More than 2 volume % of the 2nd content of the phosphazene derivative expressed with the formula (III) in the electrolytic solution from a viewpoint of "degradation-proof nature" is desirable, and its 3 - 75 volume % is more desirable. Moreover, from a viewpoint which is compatible in altitude in a low-temperature property and degradation-proof nature, 5 - 75 volume % is more desirable. If a content is said numeric-value within the limits, it can control degradation suitably.

[0065] More than 3 volume % of the 3rd content of the phosphazene derivative expressed with the formula (III) in the electrolytic solution from a viewpoint of "hypoviscosity-izing" is desirable, its 3 - 80 volume % is more desirable, and under its 3 - 50 volume % is still more desirable. Moreover, from a viewpoint which is compatible in altitude in a low-temperature property, degradation-proof nature, and hypoviscosity-ization, 5 - 80 volume % is desirable, and under 3 - 50 volume % is more desirable. A content cannot fully carry out [ hypoviscosity ]-izing of the electrolytic solution under in 3 volume %. Since the viscosity of the propylene

carbonate generally widely used for the electrolytic solution is 2.5 mPa-s (2.5 cP) and the phosphazene of  $n=3$  of this application is 0.8 mPa-s (0.8 cP), Since viscosity becomes low so that the addition of phosphazene increases, from a viewpoint of conductive improvement and improvement in a low-temperature property, it is desirable, but it is not desirable in order to cause a viscosity rise of the electrolytic solution, since supporting electrolyte solubility will be saturated, if a phosphazene addition becomes more than 50 volume %.

[0066] More than 5 volume % of the 4th content of the phosphazene derivative expressed with the formula (III) in the electrolytic solution from a viewpoint of "safety" is desirable. Since safety becomes high and the limiting oxygen index of the electrolytic solution becomes by adjusting this content more than 5 volume % more than 21 volume % so that there are many contents of phosphazene, the danger of ignition and ignition is reduced effectively. In addition, the above-mentioned oxygen-index measurement can estimate safety.

[0067] Especially the phosphazene derivative expressed with a degree type (IV) also in the phosphazene derivative of said formula (II) from a viewpoint which raises the degradation-proof nature and the safety of the electrolytic solution is desirable.

(NPR52)  $n \dots$  (IV) (the inside of a formula, and R5 -- the substituent or fluorine of monovalence -- expressing -- all -- at least one of R5 is the substituent or fluorine containing a fluorine of monovalence, and  $n$  expresses 3-8.) However, no R5 is a fluorine.

[0068] As a desirable reason, the phosphazene derivative expressed with the above-mentioned formula (IV) is as follows. that is, although self-extinguishing thru/or fire retardancy excellent in the electrolytic solution can be given and the safety of the electrolytic solution can be raised if a phosphazene derivative is contained, it expresses with a formula (IV) -- having -- all -- if at least one of R5 contains the phosphazene derivative which is the substituent of the monovalence containing a fluorine, it will become possible to give the safety which was excellent with the electrolytic solution. furthermore, it expresses with a formula (IV) -- having -- all -- if at least one of R5 contains the phosphazene derivative which is a fluorine, it will become possible to give the further excellent safety. that is, it expresses with a formula (IV) compared with the phosphazene derivative which does not contain a fluorine -- having -- all -- the phosphazene derivative which is the substituent or fluorine of monovalence with which at least one of R5 contains a fluorine has the effectiveness which make it harder to burn the electrolytic solution, and can give the safety which was further excellent to the electrolytic solution.

[0069] in addition, a formula (IV) -- setting -- all -- although the annular phosphazene derivative itself whose R5 is a fluorine and whose  $n$  is 3 is incombustibility and the effectiveness of preventing ignition at the time of flame approaching is large, since the boiling point is very low, the aprotic organic solvent left behind after they all volatilized will burn.

[0070] It is the point of an alkyl group besides an alkoxy group, an acyl group, an aryl group, a carboxyl group, etc. being mentioned, and excelling especially in improvement in the safety of the electrolytic solution as a substituent of the monovalence in a formula (IV), and an alkoxy group is suitable. It is the point of alkoxy group permutation alkoxy groups which are a methoxy group, an ethoxy radical,  $n$ -propoxy group,  $i$ -propoxy group, a butoxy radical, etc., such as an others and methoxyethoxy radical, being mentioned as an alkoxy group, and excelling in improvement in the safety of the electrolytic solution, and a methoxy group, an ethoxy radical, and especially  $n$ -propoxy group are desirable. Moreover, in respect of hypoviscosity-izing of the electrolytic solution, a methoxy group is desirable. In a formula (IV), it is the point which can give the safety excellent in the electrolytic solution as  $n$ , and 3-4 are desirable. When it is desirable that the fluorine permutes as for the substituent of said monovalence and R5 of a formula (IV) is not a fluorine as for one, the substituent of at least one monovalence is fluorine \*\*\*\*.

[0071] As a content in the phosphazene derivative of said fluorine, 3 - 70 % of the weight is desirable, and 7 - 45 % of the weight is more desirable. If a content is said numeric-value within the limits, it can do so especially suitably "the outstanding safety" which is the characteristic effectiveness of this invention.

[0072] As the molecular structure of a phosphazene derivative expressed with a formula (IV), halogens, such as chlorine and a bromine, may be included besides the above-mentioned fluorine.

[0073] By choosing suitably R5 and the  $n$  value in a formula (IV), preparation of the electrolytic solution which has the solubility suitable for more suitable safety, viscosity, and mixing etc. is attained. These phosphazene derivatives may be used by the one-sort independent, and may use two or more sorts together.

[0074] Although there will be especially no limit as viscosity of the phosphazene derivative expressed with a formula (IV) if it is below 20 mPa-s (20 cP), from a viewpoint of conductive improvement and improvement in

a low-temperature property, below 10 mPa-s (10 cP) is desirable, and below 5 mPa-s (5 cP) is more desirable.

[0075] As the flash point of the phosphazene derivative expressed with a formula (IV), although there is especially no limit, from points, such as control of ignition, its 100 degrees C or more are desirable, its 150 degrees C or more are more desirable, and its 300 degrees C or more are still more desirable. Here, this flash point serves as a scale as which flame specifically regards whenever [ breadth, and air and inclination / which forms inflammable mixture ] on a matter front face the flash point by saying wrap temperature for 75 % on this front face of the matter at least. If the phosphazene derivative has the flash point at 100 degrees C or more, even if ignition etc. is controlled and ignition etc. arises inside a cell, it will ignite and it will become possible to reduce the danger of burning and spreading on an electrolytic-solution front face.

[0076] Two kinds of contents, the 1st content which can give "degradation-proof nature" suitable for the electrolytic solution, and the 2nd content which can give "safety" excellent in especially the electrolytic solution, are mentioned by the effectiveness acquired by containing this phosphazene derivative as the total content of the phosphazene derivative expressed with the formula (IV) in the electrolytic solution.

[0077] More than 2 volume % of the 1st content of the phosphazene derivative expressed with the formula (IV) in the electrolytic solution from a viewpoint which can give "degradation-proof nature" suitably is desirable, and its 2 - 75 volume % is more desirable. If a content is said numeric-value within the limits, it can control degradation suitably.

[0078] More than 10 volume % of the 2nd content of the phosphazene derivative expressed with the formula (IV) in the electrolytic solution from a viewpoint which gives "safety" more suitably and obtains the very high lithium primary cell of safety is desirable, and more than its 15 volume % is more desirable. A content may be unable to give "safety" excellent in the electrolytic solution under by especially 10 volume %.

[0079] Moreover, from a viewpoint which is compatible in altitude in safety and degradation-proof nature, 10 - 75 volume % is more desirable, and 15 - 75 volume % is still more desirable. In addition, since the solubility of a supporting electrolyte will approach saturation and the viscosity of the electrolytic solution will rise if a phosphazene addition becomes more than 50 volume %, in order to avoid a viscosity rise of the electrolytic solution, under 50 volume % is desirable.

[0080] When the annular phosphazene derivative expressed with a formula (IV), LiBF<sub>4</sub>, gamma-butyrolactone, and/or propylene carbonate are included as the electrolytic solution from a viewpoint of "safety", especially the case where the annular phosphazene derivative and LiCF<sub>3</sub>SO<sub>3</sub> which are expressed with a formula (IV), gamma-butyrolactone, and/or propylene carbonate are included is desirable. Safety is very high, even if it is not concerned with the above-mentioned publication in these cases but a content is little. That is, in order to make the outstanding safety discover especially as a content in the electrolytic solution of the annular phosphazene derivative expressed with a formula (IV), more than 5 volume % is desirable. Moreover, it is suitable also when aiming at using it at an elevated temperature, and Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N and Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N are included as a supporting electrolyte.

[0081] As a phosphazene derivative added to an aprotic organic solvent, the phosphazene derivative which is a solid-state in 25 degrees C (ordinary temperature), and is expressed with a degree type (V) from a viewpoint which the degradation-proof nature of the electrolytic solution is raised and gives autolysis nature thru/or fire retardancy to the electrolytic solution is also desirable, controlling a viscosity rise of the electrolytic solution. (NPR62) n ... (V) (R6 expresses the substituent or halogen of monovalence among a formula.) n expresses 3-6.

[0082] As an especially desirable reason, the phosphazene derivative expressed with the above-mentioned formula (V) is as follows. Namely, it sets to the electrolytic solution containing the supporting electrolyte used as the ester system organic solvent used for the conventional lithium primary cell, and the source of a lithium ion. Although the conductivity of the electrolytic solution may fall when a supporting electrolyte decomposes with the passage of time and a decomposition product reacts with the water of the minute amount which exists in an organic solvent etc., or degradation of pole material may be produced If the phosphazene derivative expressed with a formula (V) by the conventional electrolytic solution is added, decomposition of a supporting electrolyte will be controlled and stabilization of the electrolytic solution will improve remarkably. Generally as a supporting electrolyte, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N etc. is used. LiCF<sub>3</sub>SO<sub>3</sub> with low hydrolysis of the supporting electrolyte itself, Li(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>N, Although especially Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N is desirable, LiBF<sub>4</sub> and LiPF<sub>6</sub> can be suitably used according to the above-mentioned operation of phosphazene expressed with a formula (V).



[0083] Since the phosphazene derivative expressed with a formula (V) is a solid-state in ordinary temperature (25 degrees C), if it adds to the electrolytic solution, it will dissolve in the electrolytic solution and the viscosity of the electrolytic solution will rise. However, if it is a predetermined addition as mentioned later, the viscosity R/C of the electrolytic solution will be low and will serve as a lithium primary cell which has low internal resistance and high conductivity. In addition, since the phosphazene derivative expressed with a formula (V) dissolves in the electrolytic solution, it is excellent in the long term stability of the electrolytic solution. On the other hand, if it adds exceeding a predetermined addition, the viscosity of the electrolytic solution will become remarkably large, internal resistance is high, conductivity becomes low, and it becomes impossible to use it as a lithium primary cell.

[0084] In a formula (V), as R6, if it is the substituent or halogen of monovalence, there will be especially no limit and an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. will be mentioned as a substituent of monovalence. Moreover, as a halogen, halogens, such as a fluorine, chlorine, a bromine, and iodine, are mentioned suitably, for example. An alkoxy group is desirable at the point which can control especially a viscosity rise of the electrolytic solution also in these. As this alkoxy group, a methoxy group, an ethoxy radical, a methoxyethoxy radical, a propoxy group (an isopropoxy group, n-propoxy group), a phenoxy group, a trifluoroethoxy radical, etc. are desirable, it is the point which can control a viscosity rise of the electrolytic solution, and a methoxy group, an ethoxy radical, a propoxy group (an isopropoxy group, n-propoxy group), a phenoxy group, a trifluoroethoxy radical, etc. are more desirable. As for the substituent of said monovalence, it is desirable that the above-mentioned halogen is included. In a formula (V), as n, it is the point which can control a viscosity rise of the electrolytic solution, and 3 or especially 4 is desirable.

[0085] As a phosphazene derivative expressed with a formula (V) For example, the structure where R6 is a methoxy group in said formula (V), and n is 3, The structure where a methoxy group and a phenoxy group are in any at least in a formula (V) for R6, and n is 4, The structure where R6 is an ethoxy radical in a formula (V), and n is 4, the structure where R6 is an isopropoxy group in a formula (V), and n is 3 or 4, The structure where R6 is n-propoxy group in a formula (V), and n is 4, The structure where R6 is a trifluoroethoxy radical in a formula (V), and n is 3 or 4, and the structure where R6 is a phenoxy group in a formula (V), and n is 3 or 4 are the points which can control a viscosity rise of the electrolytic solution, and are especially desirable.

[0086] By choosing suitably each substituent and n value in a formula (V), preparation of the electrolytic solution which has the solubility suitable for more suitable viscosity and mixing etc. is attained. These phosphazene derivatives may be used by the one-sort independent, and may use two or more sorts together.

[0087] It is desirable to have the substituent which contains a halogen as mentioned above as the molecular structure of a phosphazene derivative expressed with a formula (V). As this halogen, a fluorine, chlorine, a bromine, etc. are desirable and especially a fluorine is desirable. If it has the substituent which contains a halogen or a halogen in the molecular structure, it will become possible to make self-extinguishing thru/or fire retardancy discover at least more effectively of the content of a phosphazene derivative by the halogen gas guided from a phosphazene derivative. In addition, in the compound which has a substituent containing a halogen, although generating of a halogen radical may pose a problem, in order, as for the phosphazene derivative used by this invention, to form stable halogenation Lynn by the Lynn element in the molecular structure catching a halogen radical, such a problem is not generated.

[0088] As a halogen content in the phosphazene derivative of the formula (V) containing a halogen content substituent, 2 - 80 % of the weight is desirable, 2 - 60 % of the weight is more desirable, and 2 - 50 % of the weight is still more desirable. If it exceeds 80 % of the weight while the effectiveness that a content makes a halogen contain at less than 2 % of the weight may not fully show up, when it adds to the electrolytic solution, viscosity will rise, and conductivity will fall.

[0089] As the flash point of the phosphazene derivative expressed with a formula (V), although there is especially no limit, from points, such as control of ignition, its 100 degrees C or more are desirable, and its 150 degrees C or more are more desirable. If the phosphazene derivative has the flash point at 100 degrees C or more, even if ignition etc. is controlled and ignition etc. arises inside a cell, it will ignite and it will become possible to reduce the danger of burning and spreading on an electrolytic-solution front face.

[0090] As a content of the phosphazene derivative expressed with the formula (V) in the electrolytic solution According to the effectiveness acquired by containing this phosphazene derivative Four kinds of contents of the 2nd content which "viscosity rise control" of the electrolytic solution can give "degradation-proof nature"

suitable for the 1st possible content and the electrolytic solution, the 3rd content which can give "self-extinguishing" suitable for the electrolytic solution, and the 4th content which can give "fire retardancy" suitable for the electrolytic solution are mentioned.

[0091] The 1st content of the phosphazene derivative expressed with the formula (V) in the electrolytic solution from a viewpoint of "viscosity rise control" has 40 or less desirable % of the weight, its 35 or less % of the weight is more desirable, and its 30 or less % of the weight is still more desirable. It becomes [ a viscosity rise of the electrolytic solution becomes remarkably large, / internal resistance is high and / conductivity ] low and is not desirable if a content exceeds 40 % of the weight.

[0092] The 2nd content of the phosphazene derivative expressed with the formula (V) in the electrolytic solution from a viewpoint of "degradation-proof nature" has 2 desirable % of the weight or more. If a content is said numeric-value within the limits, it can control degradation suitably.

[0093] The 3rd content of the phosphazene derivative expressed with the formula (V) in the electrolytic solution from a viewpoint of "self-extinguishing" has 20 desirable % of the weight or more, from a viewpoint which is compatible in altitude in self-extinguishing and control of a viscosity rise, 20 - 40 % of the weight is more desirable, 20 - 35 % of the weight is still more desirable, and especially 20 - 30 % of the weight is desirable. A content cannot make sufficient self-extinguishing for the electrolytic solution discover at less than 20 % of the weight.

[0094] The 4th content of the phosphazene derivative expressed with the formula (V) in the electrolytic solution from a "fire-resistant" viewpoint has 30 desirable % of the weight or more, from a viewpoint which is compatible in altitude in fire retardancy and control of a viscosity rise, 30 - 40 % of the weight is more desirable, and 30 - 35 % of the weight is still more desirable. If a content is 30 % of the weight or more, it will become possible to make sufficient fire retardancy for the electrolytic solution discover of it. In addition, the above-mentioned oxygen-index measurement can estimate the self-extinguishing of the electrolytic solution thru/or fire retardancy.

[0095] When the phosphazene derivative expressed with a formula (V), LiBF<sub>4</sub>, gamma-butyrolactone, and/or propylene carbonate are included as the electrolytic solution from a viewpoint of "self-extinguishing thru/or fire retardancy", especially the case where the phosphazene derivative and LiCF<sub>3</sub>SO<sub>3</sub> which are expressed with a formula (V), gamma-butyrolactone, and/or propylene carbonate are included is desirable. It is not concerned with the above-mentioned publication in these cases, but even if said content is little, it has the outstanding self-extinguishing thru/or fire-resistant effectiveness.

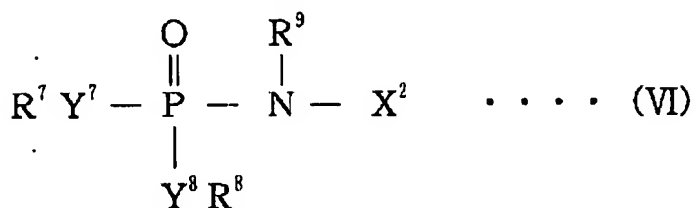
[0096] Namely, when the phosphazene derivative expressed with a formula (V), LiBF<sub>4</sub>, gamma-butyrolactone, and/or propylene carbonate are included, As a content in the electrolytic solution of this phosphazene derivative In order 5 - 10 % of the weight is desirable in order to make self-extinguishing discover, and to make fire retardancy discover The amount exceeding 10 % of the weight is desirable, 40 or less % of the weight is more desirable, and it exceeds 10 % of the weight, and 35 or less % of the weight is still more desirable, it exceeds [ from a viewpoint which is compatible in altitude in fire retardancy and control of a viscosity rise it exceeds 10 % of the weight, and ] 10 % of the weight, and especially 30 or less % of the weight is desirable.

[0097] Moreover, when the phosphazene derivative and LiCF<sub>3</sub>SO<sub>3</sub> which are expressed with a formula (V), gamma-butyrolactone, and/or propylene carbonate are included, As a content in the electrolytic solution of this phosphazene derivative In order 5 - 25 % of the weight is desirable in order to make self-extinguishing discover, and to make fire retardancy discover The amount exceeding 25 % of the weight is desirable, 40 or less % of the weight is more desirable, and it exceeds 25 % of the weight, and 35 or less % of the weight is still more desirable, it exceeds [ from a viewpoint which is compatible in altitude in fire retardancy and control of a viscosity rise it exceeds 25 % of the weight, and ] 25 % of the weight, and especially 30 or less % of the weight is desirable.

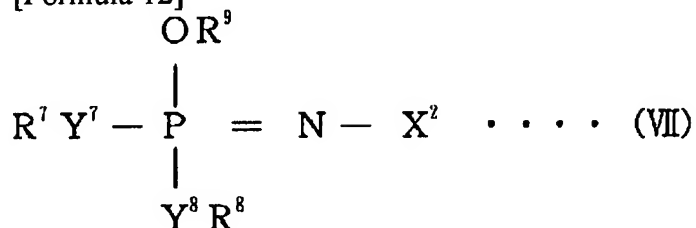
[0098] Especially as an isomer of the phosphazene derivative added to an aprotic organic solvent, although not restricted, the low-temperature property of a lithium primary cell is raised, autolysis nature thru/or fire retardancy are given to the electrolytic solution, and the isomer of the phosphazene derivative which is expressed with a degree type (VI) and is expressed with a degree type (VII) from a viewpoint which raises the degradation-proof nature of the electrolytic solution is still more desirable.

[Formula 11]





[Formula 12]



(Formula (VI) And (VII) it sets and R7, R8, and R9 express the substituent or halogen of monovalence.) X2 expresses carbon, silicon, germanium, tin, nitrogen, Lynn, an arsenic, antimony, a bismuth, oxygen, sulfur, a selenium, a tellurium, and the substituent containing at least one sort of the element chosen from the group which consists of a polonium. Y7 and Y8 express a divalent connection radical, a divalent element, or single bond.

[0099] The isomer of the phosphazene derivative which is expressed with a formula (VI) and expressed with a formula (VII) is as follows as a desirable reason. Namely, the isomer of the phosphazene derivative which is expressed with a formula (VI) and expressed with a formula (VII) has only the potential window which fully functions as a primary cell, and does not decompose it by discharge. Moreover, since the self-extinguishing thru/or fire retardancy which was excellent in the electrolytic solution with an operation of the nitrogen gas guided from this isomer, halogen gas, etc. is given, as for the lithium primary cell containing this electrolytic solution, safety becomes high. Furthermore, since the isomer of the phosphazene derivative which is expressed with a formula (VI) and expressed with a formula (VII) contains a halogen (for example, fluorine), it functions also as a scavenger of an activity radical at the time of emergency combustion, and an organic substituent also has the screening effect of oxygen in order to generate carbide (char) on pole material and a separator at the time of combustion. In addition, also when a user charges accidentally, since this isomer has the depressor effect of dendrite generation, as compared with an additive-free system, safety becomes higher. Furthermore, since Lynn has the operation which controls chain decomposition of the polymeric materials which constitute a cell, self-extinguishing thru/or fire retardancy are discovered effectively.

[0100] Moreover, it sets to the electrolytic solution containing the supporting electrolyte used as the ester system organic solvent used for the conventional lithium primary cell, and the source of a lithium ion. Although the conductivity of the electrolytic solution may fall when a supporting electrolyte decomposes with the passage of time and a decomposition product reacts with the water of the minute amount which exists in an organic solvent etc., or degradation of pole material may be produced If the phosphazene derivative expressed with the isomer expressed with a formula (VI) by the conventional electrolytic solution and a formula (VII) is added, decomposition of a supporting electrolyte will be controlled and it will contribute to stabilization of the electrolytic solution remarkably. Generally as a supporting electrolyte, LiBF4, LiPF6, LiCF3SO3, Li(C2F5SO2) 2N, Li(CF3SO2) 2N etc. is used. LiCF3SO3 with low hydrolysis of the supporting electrolyte itself, Li(C2F5SO2) 2N, Although especially Li(CF3SO2)2N is desirable, LiBF4 and LiPF6 can be suitably used according to the above-mentioned operation of this isomer and phosphazene.

[0101] Furthermore, the isomer of the phosphazene derivative which is expressed with a formula (VI) and expressed with a formula (VII) may make the low-temperature property which was extremely excellent in the electrolytic solution discover, when added by the electrolytic solution.

[0102] As R7, R8, and R9 in a formula (VI), if it is the substituent or halogen of monovalence, there will be especially no limit and an alkoxy group, an alkyl group, a carboxyl group, an acyl group, an aryl group, etc. will be mentioned as a substituent of monovalence. Moreover, as a halogen, halogens, such as a fluorine, chlorine, and a bromine, are mentioned suitably, for example. Also in these, a fluorine, an alkoxy group, etc. are especially desirable in respect of the low-temperature property of the electrolytic solution, and electrochemical

stability. Moreover, the alkoxy group containing a fluorine, an alkoxy group, a fluorine, etc. is desirable in respect of hypoviscosity-izing of the electrolytic solution. The substituent of the same class is sufficient as all of R7-R9, and the substituent of the class from which some of them differ is sufficient as them.

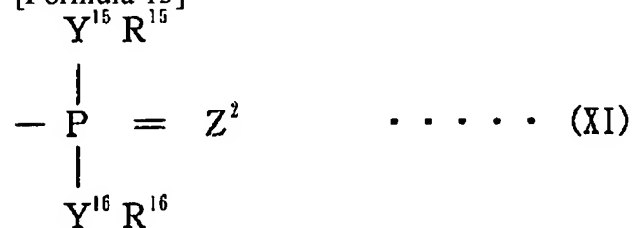
[0103] As an alkoxy group, alkoxy permutation alkoxy groups, such as a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. and a methoxyethoxy radical, a methoxyethoxy ethoxy radical, etc. are mentioned, for example. Also in these, all are suitable for a methoxy group, an ethoxy radical, a methoxyethoxy radical, or a methoxyethoxy ethoxy radical as R7-R9, and it is suitable that the viewpoint of hypoviscosity and a quantity dielectric constant to all are especially a methoxy group or an ethoxy radical. As an alkyl group, a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, etc. are mentioned. As an acyl group, a formyl group, an acetyl group, a propionyl radical, a butyryl radical, an isobutyryl radical, a valeryl radical, etc. are mentioned. As an aryl group, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As for the hydrogen element in these substituents, permuting by the halogen is desirable, and a fluorine, chlorine, a bromine, etc. are suitably mentioned as a halogen.

[0104] In a formula (VI), as a divalent connection radical expressed with Y7 and Y8 For example, oxygen besides two CH(s), sulfur, a selenium, nitrogen, boron, aluminum, A scandium, a gallium, an yttrium, an indium, a lanthanum, a thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Lynn, Vanadium, an arsenic, niobium, antimony, a tantalum, a bismuth, chromium, The divalent connection radical containing at least one sort of the element chosen from the group which consists of molybdenum, a tellurium, a polonium, a tungsten, iron, cobalt, and nickel is mentioned. The divalent connection radical containing at least one sort of the element chosen from the group which consists of two CH(s) and oxygen, sulfur, a selenium, and nitrogen also in these is desirable. Moreover, Y7 and Y8 may be divalent elements, such as oxygen, sulfur, and a selenium, or single bond. Especially a sulfur element is desirable in the divalent connection radical which contains the element of sulfur and/or oxygen at the point whose fire retardancy of the electrolytic solution improves, an oxygen element, and a list, and the divalent connection radical which contains an oxygen element in that it excels in the low-temperature property of the electrolytic solution, and especially an oxygen element are desirable. The same class is sufficient as Y7 and Y8, and a mutually different class is sufficient as them.

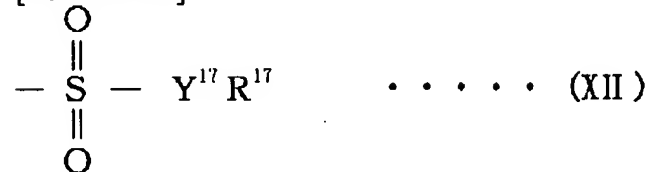
[0105] As X2, from a viewpoint of consideration of harmful nature, an environment, etc., the substituent containing at least one sort of carbon, silicon, nitrogen, Lynn, oxygen, and the element chosen from the group which consists of sulfur is desirable, and the substituent which has a degree type (XI) or (XII) (XIII) the structure expressed is more desirable in a formula (VI).

[0106]

[Formula 13]



[Formula 14]



[Formula 15]



[0107] However, in a formula (XI), (XII), and (XIII), R15-R19 express the substituent or halogen of monovalence. Y15-Y19 express a divalent connection radical, a divalent element, or single bond, and Z2 expresses a divalent radical or a divalent element.

[0108] In a formula (XI), (XII), and (XIII), each the substituent or halogen of the same monovalence is mentioned suitably as R7-R9 in a formula (VI) described as R15-R19. Moreover, the class from which the respectively same class is sufficient and some differ mutually in the same substituent is sufficient as these. It may join together mutually and R15 and R16 of a formula (XI), and R18 and R19 of a formula (XIII) may form the ring.

[0109] In a formula (XI), (XII), and (XIII), the same divalent connection radical or same divalent element etc. is mentioned, and similarly, when it is the divalent connection radical and oxygen element containing the element of sulfur and/or oxygen, or a sulfur element, especially since the fire retardancy of the electrolytic solution improves, it is as desirable as Y7-Y8 in a formula (I) described as a radical expressed with Y15-Y19. Moreover, the divalent connection radical which contains an oxygen element in that it excels in the low-temperature property of the electrolytic solution, and especially an oxygen element are desirable. The class from which the respectively same class is sufficient and some differ mutually in the same substituent is sufficient as these.

[0110] It sets at a ceremony (XI) and they are two CH(s) and CHR (R expresses an alkyl group, an alkoxyl group, a phenyl group, etc.) as Z2, for example. the following -- the same . oxygen besides a radical and NR radical, sulfur, a selenium, boron, and aluminum -- A scandium, a gallium, an yttrium, an indium, a lanthanum, a thallium, Carbon, silicon, titanium, tin, germanium, a zirconium, lead, Linn, Vanadium, an arsenic, niobium, antimony, a tantalum, a bismuth, chromium, The divalent radical containing at least one sort of the element chosen from the group which consists of molybdenum, a tellurium, a polonium, a tungsten, iron, cobalt, and nickel etc. is mentioned. The divalent radical containing at least one sort of the element chosen from the group which consists of oxygen besides two CH(s), a CHR radical, and NR radical, sulfur, and a selenium also in these is desirable. Moreover, Z2 may be divalent elements, such as oxygen, sulfur, and a selenium. When it is the divalent radical and sulfur element which contain sulfur and/or a selenium element especially, or a selenium element, since the fire retardancy of the electrolytic solution improves, it is desirable. Moreover, the divalent radical which contains an oxygen element in that it excels in the low-temperature property of the electrolytic solution, and especially an oxygen element are desirable.

[0111] It is the point which may discover self-extinguishing thru/or fire retardancy effectively especially as these substituents, and especially a substituent including Linn which is expressed with a formula (XI) is desirable. Furthermore, in a formula (XI), especially when Z2, Y15, and Y16 are oxygen elements, it becomes possible to make the low-temperature property which was extremely excellent in the electrolytic solution discover. Moreover, especially when a substituent is a substituent containing sulfur which is expressed with a formula (XII), it is desirable in respect of the formation of small interfacial resistance of the electrolytic solution.

[0112] Preparation of the electrolytic solution which has more suitable viscosity, the solubility suitable for addition and mixing, a low-temperature property, etc. is attained by choosing suitably R7-R9 in a formula (VI) and (XI) - (XIII), R15-R19, Y7-Y8, Y15-Y19, and Z2. These compounds may be used by the one-sort independent, and may use two or more sorts together.

[0113] The isomer expressed with a formula (VI) can be manufactured by adjusting the degree of vacuum and/or temperature at the time of generating the phosphazene derivative which is an isomer of the phosphazene derivative expressed with a formula (VII), for example, is expressed with a formula (VII), and the content (volume %) in the electrolytic solution of this isomer can be measured with the following measuring method. A mole ratio is obtained by comparing with the area per mol of said isomer which asked for the peak area of a sample and asked for this peak area beforehand with <<measuring method>> gel permeation chromatography (GPC) or high performance chromatography, and it can measure by carrying out volume conversion in consideration of specific gravity further.

[0114] As a phosphazene derivative expressed with a formula (VII), viscosity is comparatively low and what may dissolve a supporting electrolyte good is desirable. As R7-R9 of a formula (VII), Y7-Y8, and X2, all of that explanation of R7-R9 of a formula (VI), Y7-Y8, and X2 described and the same thing are mentioned suitably.

[0115] As the flash point of the phosphazene derivative expressed with a formula (VII), although there is especially no limit, from points, such as control of ignition, its 100 degrees C or more are desirable, and its 150 degrees C or more are more desirable. If the phosphazene derivative has the flash point at 100 degrees C or more, even if ignition etc. is controlled and ignition etc. arises inside a cell, it will ignite and it will become possible to reduce the danger of burning and spreading on an electrolytic-solution front face.

[0116] It is desirable to have a substituent containing a halogen as the molecular structure of a phosphazene derivative expressed with the isomer and formula (VII) which are expressed with a formula (VI). As this halogen, a fluorine, chlorine, a bromine, etc. are desirable and especially a fluorine is desirable. If it has the substituent which contains a halogen in the molecular structure, it will become possible to make self-extinguishing thru/or fire retardancy discover at least more effectively of the content of these matter by the halogen gas guided. In addition, in the compound which has a substituent containing a halogen, although generating of a halogen radical may pose a problem, in order that the Lynn element in the molecular structure may catch a halogen radical and may form stable halogenation Lynn, such a problem is not generated in said isomer and a phosphazene derivative.

[0117] As a content in the isomer and phosphazene derivative of a halogen, 2 - 80 % of the weight is desirable, 2 - 60 % of the weight is more desirable, and 2 - 50 % of the weight is still more desirable. Since viscosity will become high if it exceeds 80 % of the weight while the effectiveness that a content makes a halogen contain at less than 2 % of the weight may not fully show up, when it adds to the electrolytic solution, the conductivity may fall.

[0118] As the total content with the phosphazene derivative expressed with the isomer expressed with the formula (VI) in the electrolytic solution, and a formula (VII) According to the effectiveness acquired by containing this isomer and this phosphazene derivative The 1st content which can give a "low-temperature property" suitably with the electrolytic solution, the 2nd content which can give "degradation-proof nature" suitable for the electrolytic solution, Four kinds of contents of the 3rd content which can give "self-extinguishing" suitable for the electrolytic solution, and the 4th content which can give "fire retardancy" suitable for the electrolytic solution are mentioned.

[0119] More than 1 volume % of the 1st content with the phosphazene derivative expressed with the isomer expressed with the formula (VI) in the electrolytic solution and a formula (VII) from a viewpoint of a "low-temperature property" is desirable, more than its 2 volume % is more desirable, and more than its 5 volume % is still more desirable. Unless a content fulfills 1 volume %, the low-temperature property of the electrolytic solution is not enough.

[0120] More than 2 volume % of the 2nd content with the phosphazene derivative expressed with the isomer expressed with the formula (VI) in the electrolytic solution and a formula (VII) from a viewpoint of "degradation-proof nature" is desirable, and its 3 - 75 volume % is more desirable. Moreover, from a viewpoint which is compatible in altitude in degradation-proof nature and a low-temperature property, 5 - 75 volume % is more desirable. If a content is said numeric-value within the limits, it can control degradation suitably.

[0121] More than 20 volume % of the 3rd content with the phosphazene derivative expressed with the isomer expressed with the formula (VI) in the electrolytic solution and a formula (VII) from a viewpoint of "self-extinguishing" is desirable. A content cannot make sufficient self-extinguishing for the electrolytic solution discover under by 20 volume %.

[0122] More than 30 volume % of the 4th content with the phosphazene derivative expressed with the isomer expressed with the formula (VI) in the electrolytic solution and a formula (VII) from a "fire-resistant" viewpoint is desirable. If a content is more than 30 volume %, it will become possible to make sufficient fire retardancy for the electrolytic solution discover of it.

[0123] When the phosphazene derivative expressed with the isomer and formula (VII) which are expressed with a formula (VI) as the electrolytic solution from a viewpoint of "self-extinguishing thru/or fire retardancy",  $\text{LiBF}_4$ , and the gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included, especially the case where the phosphazene derivative expressed with the isomer and formula (VII) which are expressed with a formula (VI),  $\text{LiCF}_3\text{SO}_3$ , and the gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included is desirable. It is not concerned with the above-mentioned publication in these cases, but even if the content in the electrolytic solution of an isomer and a phosphazene derivative is little, it has the outstanding self-extinguishing thru/or fire-resistant effectiveness.

[0124] That is, when the phosphazene derivative expressed with the isomer and formula (VII) which are expressed with a formula (VI),  $\text{LiBF}_4$ , and the gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included, as the total content in the electrolytic solution of this isomer and this phosphazene derivative, in order to make fire retardancy discover, the amount exceeding 10 volume % is desirable [ in order to make self-extinguishing discover, 1.5 - 10 volume % is desirable, and ]. Moreover, when the phosphazene derivative expressed with the isomer and formula (VII) which are expressed with a formula (VI),  $\text{LiCF}_3\text{SO}_3$ , and the gamma-butyrolactone and/or propylene carbonate more than 45 volume % are included, as the total content in the electrolytic solution of this isomer and this phosphazene derivative, in order to make fire retardancy discover, the amount exceeding 15 volume % is desirable [ in order to make self-extinguishing discover, 2.5 - 15 volume % is desirable, and ].

[0125] The separator made to intervene between forward negative electrodes in a lithium primary cell by the role which prevents the short circuit of the current by contact of two poles as other members used for the lithium primary cell of this invention is mentioned. The nonwoven fabric made of synthetic resin, such as the ingredient which can prevent contact of two poles certainly, and, and contains or is made as the quality of the material of a separator, for example, polytetrafluoroethylene, polypropylene, polyethylene, a cellulose system, polybutylene terephthalate, and polyethylene terephthalate, a thin layer film, etc. are mentioned suitably. [ letting the electrolytic solution pass ] Also in these, especially films, such as polypropylene with a thickness of about 20-50 micrometers or a microporous film made from polyethylene, a cellulose system, polybutylene terephthalate, and polyethylene terephthalate, are suitable. In this invention, the well-known each part material usually used for the cell other than an above-mentioned separator can use it suitably.

[0126] As a gestalt of the lithium primary cell of this invention explained above, there is especially no limit and various well-known gestalten, such as a cylindrical cell of a coin type, a carbon button type, a paper type, a square shape, or spiral structure, are mentioned suitably. In a carbon button type case, sheet-like a positive electrode and a negative electrode can be produced, and it can produce a lithium primary cell by inserting a separator with this positive electrode and a negative electrode etc. Moreover, the positive electrode of the shape for example, of a sheet is produced, in the case of spiral structure, a charge collector can be inserted, and it can produce a lithium primary cell by piling up and winding up a negative electrode (the shape of a sheet) to this etc.

[0127] Since it is desirable that the particle of a very detailed metallic oxide is distributed between the particles of a manganese dioxide as for the positive electrode for the lithium primary cells of this invention, a metallic oxide is preferably prepared with a sol gel process. In addition, if only it can prepare a very detailed particle, especially the method of preparation is not restricted.

[0128] The positive electrode used for the lithium primary cell of this invention can be manufactured according to the following 1st thru/or the 4th following process. At the 1st process, the alkoxide of at least one sort of metals chosen from the group which consists of a manganese dioxide, titanium and aluminum, zinc, chromium, a lithium, nickel, copper, and iron into an organic solvent is added, it mixes, and mixed liquor is prepared. As an organic solvent, low-boiling point ketones, such as low-boiling point alcohol, such as a methanol and ethanol, or an acetone, are desirable, and especially ethanol is desirable. As an alkoxy group [ in / on the other hand / a metal alkoxide ], the isopropoxy group from a soluble viewpoint of a metal alkoxide over an organic solvent, n-propoxy group, etc. are desirable.

[0129] At the 2nd process, water is added to the mixed liquor prepared at the 1st process, and the hydrolysis reaction of said metal alkoxide generates the metal hydroxide corresponding to this metal alkoxide. In addition, as for the 2nd process, it is desirable to carry out ice-cooling.

[0130] Next, by heating and drying the liquid containing a metal hydroxide at the 3rd process, a metal hydroxide is used as a metallic oxide, removing a solvent, and the powder for positive electrodes which distributed this metallic oxide between manganese-dioxide particles is manufactured. In addition, in order to perform removal and dehydration of a solvent completely, as for heating and desiccation, it is desirable to carry out time sufficient at the temperature of 120-300 degrees C.

[0131] Next, the powder for positive electrodes obtained at the 3rd process is fabricated in a predetermined configuration at the 4th process, and the positive electrode for lithium primary cells is obtained at it. The shaping approach will not be limited especially if the positive electrode of the reinforcement of extent which is not damaged in the manufacture process of a lithium primary cell can be fabricated, but a well-known approach

can be conventionally used for it. For example, it can carry out also by piercing said powder for positive electrodes and piercing by the opportunity with the mold corresponding to the configuration of the positive electrode of the target lithium primary cell. In addition, after mixing and kneading additives, such as the above-mentioned electric conduction material and a binder, making them into the shape of a paste and carrying out hot air drying (100-120 degrees C) to the powder for positive electrodes before shaping, you may pierce with a punching machine.

[0132]

[Example] Although an example is given to below and this invention is explained to it in more detail, this invention does not have the range limited by these examples.

[0133] (Example 1) The positive electrode for lithium primary cells was produced by the following approach. Ethanol Into 10mL, titanium isopropoxide (Ti [OCH (CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>) 0.07g (0.25mmol) is added, and it agitated for 30 minutes and was made to dissolve under atmospheric air. Next, agitating, 1g (Mitsui Mining EMD) of manganese dioxides was added, and the generated ethanol solution was distributed. Next, it is water to this, ice-cooling these dispersion liquid. 0.5mL (27mmol) was added and, thereby, titanium isopropoxide was used as hydroxylation titanium (Ti<sub>4</sub> (OH)). Next, stoving of the mixed liquor containing the generated hydroxylation titanium was carried out at 80 degrees C, further, by drying at 300 degrees C for 1 hour, hydroxylation titanium was used as titanium oxide and the powder with which this titanium oxide was distributed between manganese-dioxide particles was obtained. Thus, the obtained powder was taught to the oven of a glass tube, and it dehydrated at 100 degrees C for 1 hour, and was made the powder for positive electrodes. The mass of the titanium oxide in the powder for positive electrodes was 2% to the mass of a manganese dioxide.

[0134] After 8:1:1 having mixed and kneaded comparatively (mass ratio) this powder for positive electrodes, acetylene black, and polytetrafluoroethylene (PTFE) and carrying out coating of this kneading object with a doctor blade, the positive electrode for lithium primary cells was produced by starting what carried out hot air drying (100-120 degrees C), and was obtained with phi 16mm punching machine. In addition, the mass of a positive electrode is 19mg. The lithium primary cell was produced as follows using this positive electrode.

[0135] In addition, what pierced the lithium foil (thickness of 0.5mm) to phi 16mm was used for the negative electrode, and the nickel foil was used for the charge collector. Moreover, the electrolytic solution is the phosphazene derivative A (in said formula (IV)). The annular phosphazene derivative compound whose n is 3 and whose four two are an ethoxy radical and are a fluorine among six R, and viscosity:1.2 mPa-s (1.2 cP) 10 volume % in 25 degrees C, It prepared by dissolving LiBF<sub>4</sub> (lithium salt) in a mixed solution with gamma-butyrolactone (GBL) 90 volume % by the concentration of 0.75 mol/L (M).

[0136] Used the cellulose separator (TF4030 by the Japanese altitude paper-making business company) as a separator, the above-mentioned forward negative electrode was made to sit opposite to each other through this, the above-mentioned electrolytic solution was poured in and obturated, and the lithium primary cell of CR2016 mold was produced.

[0137] The cell property of the lithium primary cell of this example was searched for with the following test method, and was compared with the general-purpose lithium primary cell as a conventional example. Titanium oxide is not distributed between manganese-dioxide particles, and the mass of a positive electrode is 19mg, and a general-purpose lithium primary cell has the same structure as the lithium primary cell of an example 1 except having used the electrolytic solution which was made to dissolve LiBF<sub>4</sub> (lithium salt) in gamma-butyrolactone (GBL) by the concentration of 0.75 mol/L (M), and was prepared.

[0138] The ordinary temperature discharge curve which discharges to 1.5V (minimum electrical potential difference) by 1mA (0.2C) constant current under 25-degree C atmospheric air, and shows these cells to drawing 1 was obtained. A continuous line shows the discharge curve of an example 1 among drawing, and a dotted line shows the discharge curve of the conventional example.

[0139] When discharge capacity was calculated from the discharge curve of drawing 1, the discharge capacity of an example 1 was 298 mAh/g, and was 235 mAh/g in the conventional example.

[0140] Furthermore, when it integrated with the charging-time-value-electrical-potential-difference curve and asked for energy density based on the discharge curve of drawing 1, the energy density of an example 1 was 726 Wh/kg, and was 583 Wh/kg in the conventional example.

[0141] Moreover, the limiting oxygen index of the electrolytic solution of an example 1 and the conventional example was measured according to JIS K 7201. Consequently, in the electrolytic solution of an example 1, the



limiting oxygen index was 25.1 volume %, and it was 17.1 volume % in the electrolytic solution of the conventional example.

[0142] (Examples 2-3 and examples 1-2 of a comparison) Except changing the amount of the titanium oxide distributed between manganese-dioxide particles like a Table 1 publication, the powder for positive electrodes was prepared like the example 1, and the lithium primary cell was produced. To the obtained lithium primary cell, measurement of discharge capacity and energy density is performed like an example 1, and the result is shown in Table 1.

[0143]

[Table 1]

	単位	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
酸化チタンの量	質量%	2	0.5	4	0.3	5
放電容量	mAh/g	298	290	288	240	260
エネルギー密度	Wh/kg	726	719	704	619	652

[0144] (Example 4) Except having distributed the zinc oxide between the particles of a manganese dioxide instead of titanium oxide (the mass of the zinc oxide to the mass of a manganese dioxide being 2%), the lithium primary cell was produced like the example 1, and discharge capacity and energy density were measured similarly. Consequently, discharge capacity was 295 mAh/g and energy density was 720 Wh/kg.

[0145] (Example 5) It is the phosphazene derivative B (in said formula (IV)) instead of the phosphazene derivative A. The annular phosphazene derivative compound whose n is 3 and whose five one is a methoxy group and are a fluorine among six R, Viscosity in 25 degrees C: Except having used 1.8 mPa-s (1.8 cP), the electrolytic solution was prepared like the example 1, the lithium primary cell was produced, and discharge capacity and energy density were measured similarly. Consequently, discharge capacity was 297 mAh/g and energy density was 725 Wh/kg. Moreover, when the limiting oxygen index of the electrolytic solution was measured like the example 1, the limiting oxygen index was 25.0 volume %.

[0146] (Example 6) It is the phosphazene derivative C (in said formula (IV)) instead of the phosphazene derivative A. The annular phosphazene derivative compound whose n is 4 and whose seven one is an ethoxy radical and are a fluorine among eight R, Viscosity in 25 degrees C: Except having used 1.3 mPa-s (1.3 cP), the electrolytic solution was prepared like the example 1, the lithium primary cell was produced, and discharge capacity and energy density were measured similarly. Consequently, discharge capacity was 295 mAh/g and energy density was 720 Wh/kg. Moreover, when the limiting oxygen index of the electrolytic solution was measured like the example 1, the limiting oxygen index was 25.8 volume %.

[0147] By distributing titanium oxide between manganese-dioxide particles, adding a phosphazene derivative, and preparing the electrolytic solution from these results, shows that discharge capacity and energy density improve remarkably, and the limiting oxygen index of the electrolytic solution rises and safety improves greatly.

[0148]

[Effect of the Invention] According to this invention, by constituting a lithium primary cell using the positive electrode which consists of powder which distributed the specific metallic oxide, and the electrolytic solution which added the isomer of a phosphazene derivative and/or a phosphazene derivative between the particles of a manganese dioxide, since discharge capacity and the energy density are high, a lithium primary cell with high safety can be offered long lasting by high power.

[Translation done.]